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The influence of lithium carbonate on phase composition of calcium aluminate cement paste

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Abstract

In the paper the results of experiment are presented which main goal was to examine the influence of lithium carbonate addition on the phase composition development of calcium aluminate cement. The study shows that the lithium carbonate has the significant influence on the reaction rate of alumina cement components and water. Very little addition of admixture (as 0.03%) causes the X-ray identifiable effect on calcium aluminate hydrates after 15 minutes mixing with water. Hydration products in the presence of lithium carbonate differ from the phases that occur in the case of alumina cement binder without the admixture. The article shows the test results for the monocalcium aluminate. A significant impact on the course of the hydration reaction is also confirmed by the results of calorimetric look into alumina cement and monocalcium aluminate paste.

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1. Introduction

Rapid development of production technology and increase of requirements regarding special mortars lead to constant search for modification possibility of traditionally used binders. The use of alumina cement in the

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production of building mortars results mainly from a high speed of strength development. For instance, in the case of type F tile adhesives according to PN-EN 12004 a rapid strength development of mortar is required to achieve high bond strength after short hardening time. It corresponds to the tensile strength of at least 0,5 MPa after 6 hours since mixing of adhesive with water.

In practice the mixtures of alumina cement and Portland cement are the most frequently used binders in type F tile adhesives. As indicated by Kurdowski [1], Bensted [2], Neville [3], Robson [4] the mixing of Portland cement with alumina cement is possible only in specified proportions. The rapid setting may occur when the content of one of the cements in the mixture is 20-80 % [2]. Setting time of Portland cement and alumina cement paste is shorter when the content ratio of particular cement in the mixture is higher.

However, the use of admixtures in the production of cement based adhesives, i.e. methylcellulose, redispersible powders and others leads to the significant extension of setting time. Setting time and speed of strength development of mortar, even in the case of alumina cement and Portland cement mixture with 1:1 proportion is too low. In order to obtain required early bond strength it is necessary to use additionally admixtures accelerating the setting of binder.

Literature concerning possibility of acceleration of setting and hardening of Portland cement is very extensive, e.g. Kurdowski [1], Bensted [2], Neville [3], Robson [4]. In the case of alumina cement the situation is different. According to Bensted [4] lithium salts, sodium and potassium hydroxides, Portland cement, calcium oxide and calcium sulphate hemihydrate strongly influence on the hydration of alumina cement. However, influence of little addition of alkali metals salts on the properties of alumina cement pastes and mortars is a subject of few investigations Matusinović and Vrbos [7], Venuat [8], Niziurska and Małolepszy [9]. Researches of Matusinović and Vrbos [7] and Venuat [8] concern the setting time and strength of alumina cement mortar in the period from 20 hours since mixing with water. They indicate that the shortest setting time and the highest acceleration of alumina cement hardening is achieved when lithium salt is used. The results published by Niziurska and Małolepszy [9] confirm a high influence of lithium carbonate on the acceleration of setting and hardening of mortars made of alumina cement.

2. Literature discussion

2.1. Hydration of alumina cement

Calcium monoaluminate CA is the most important phase in alumina cement. CA crystallizes to monoclinic system and its typical content in alumina cement is 60 – 70 %.

As indicated by Bensted [2] depending on the temperature of CA hydration four hydrates may form: CAH_{10} , C_2AH_8 , C_3AH_6 , C_4AH_{13} . CAH_{10} is formed at temperatures below 15 °C, while above 15 °C, up to about 25 °C, CA is hydrated with formation of CAH_{10} and C_2AH_8 mixture, while the amount of the second hydrate increases with temperature increase. At higher temperatures, above 25 °C, C_2AH_8 becomes a hydration product together with hydrated aluminum oxide, initially gel-like, afterwards crystallizing to gibbsite AH_3 . Above 40 °C calcium monoaluminate is hydrating to C_3AH_6 hydrogarnets and hydrated aluminum oxide, eventually crystallizing to gibbsite.

Hydrocalumite C_4AH_{13} is a hydration product of the lowest content that furthermore is not relevant in the aspect of setting and early strength. According to Bensted [2] higher amounts of hydrocalumite are observed in hydrated cement pastes activated by lithium carbonate or chloride.

Calcium aluminoferrite (brownmillerite) C_4AF is the second important phase in alumina cement and its typical content in cement is 15 - 40 %. Due to the resistance of alumina cement to sulphate corrosion the presence of calcium aluminoferrite is favorable because it does not promote ettringite formation. Simultaneously the lower

conversion speed of hydrates comparing to hydrates from CA inhibits an increase of porosity and permeability, thus limits a decrease of compressive strength too.

Mayenite $C_{12}A_7$ is a next phase present in alumina cement, normally in quantity of 2-5 %. As a separate phase it binds with water rapidly. Mayenite increases reactivity of calcium monoaluminate, thus ensures proper setting of alumina cement.

Besides highly hydraulic phases discussed above there are also phases of weak hydraulic properties in alumina cement, such as gehlenite C_2AS and pleochroite (glassy phase). Gehlenite reacts slowly with formation of stratlingite – hydrated calcium aluminosilicate C_2ASH_8 . Stratlingite is a stable hydrate of importance in terms of late strength of alumina cement. Formation of pleochroite during burning process of alumina clinker takes place due to highly reducing conditions. That formation is not desirable because it takes place at the expense of intended CA phase. Hydration of pleochroite leads to the formation of hydrated calcium aluminates and also little amounts of C-S-H and stratlingite.

Conversions taking place during hydration of alumina cement are connected with thermal effects which take place in the following stages: evolution of significant amounts of heat in the first minutes after mixing with water – the heat of wetting, induction period – next 2-3 hours and afterwards acceleration of reaction related to the evolution of significant amount of heat due to the crystallization that is almost completely finished during 24 hours as stated by Kirca [10].

2.2. Conversion of calcium aluminate hydrates

Hexagonal crystals of CAH_{10} , C_2AH_8 , C_4AH_{13} are metastable phases and are converted over time into C_3AH_6 hydrogarnet. That conversion leads to the increase of porosity and permeability, thus to relevant strength decrease. According to Bensted [2] that effect can be limited by keeping the water to cement ratio below 0.4. Moreover according to Kirca [10] the speed of conversion of hydrated calcium aluminates depends on the temperature. At around 20 °C that process may last even couple of years, while at 50 °C it may occur after several dozen of hours. The author also confirms the influence of higher water to cement ratio and higher humidity during hydration on the acceleration of conversion speed of hydrates.

2.3. Hydration of alumina cement in the presence of lithium ions

There is few information in the literature regarding influence of lithium ions on the hydration process of alumina cement. According to Goetz – Neunhoffer [11] introduction of Li^+ ion leads to the precipitation of LA_2H_{10} in the paste that being a transition phase prevents formation of impermeable coating on CA grains. Substitution of Li^+ ions by Ca^{2+} ions leads to the crystallization of C_2AH_8 and CAH_{10} , while free Li^+ cation forms LA_2H_{10} transition phase again.

3. Experiment

3.1. Scope

In order to evaluate influence of lithium ions introduced by carbonate on the hydration of alumina cement the phase composition has been investigated by XRD method and the heat of hydration tests have been performed. Alumina cement without and with 0.3% addition of lithium carbonate (related to binder mass), chosen based on the previous tests of setting time and strength, were the objects of the research. Moreover the investigation included calcium monoaluminate (CA) synthesized at the laboratory. Phase composition examinations have been initially conducted with intervals of 15 minutes, afterwards every 0.5 hour up to 6 hours and finally every 1 hour up to 24

hours. The surface of hydrating sample was protected by waterproof polymer foil introducing single wide peak to the registered XRD patterns.

3.2. Materials

Phase composition of alumina cement (G40) and calcium aluminate (CA) used in the study is presented in Fig. 1 and 2 respectively. Lithium carbonate (Li_2CO_3) of analytical grade was used as an admixture.

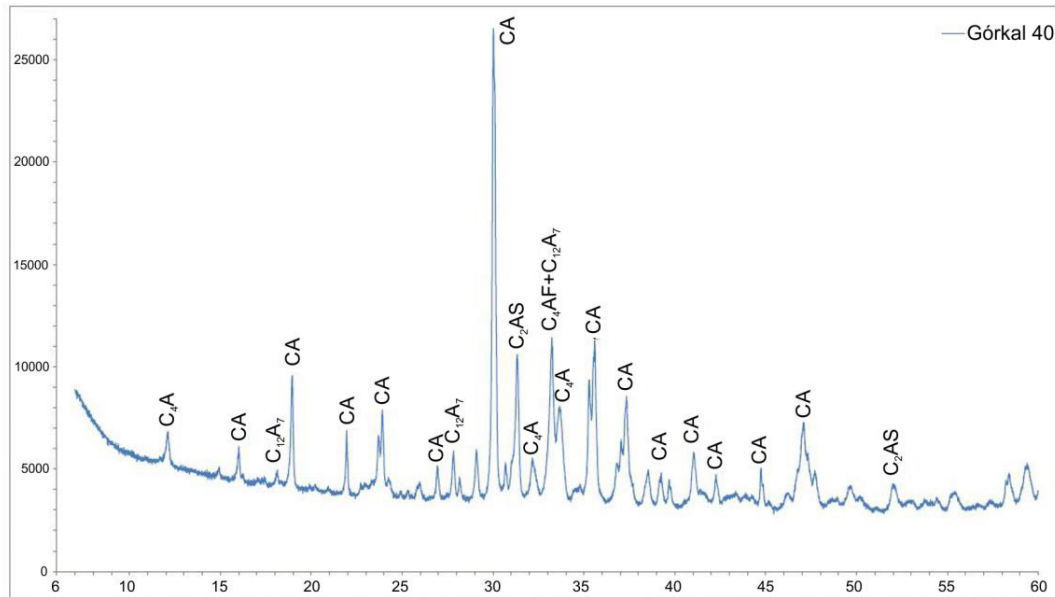


Fig. 1. XRD pattern of Górkal 40 alumina cement.

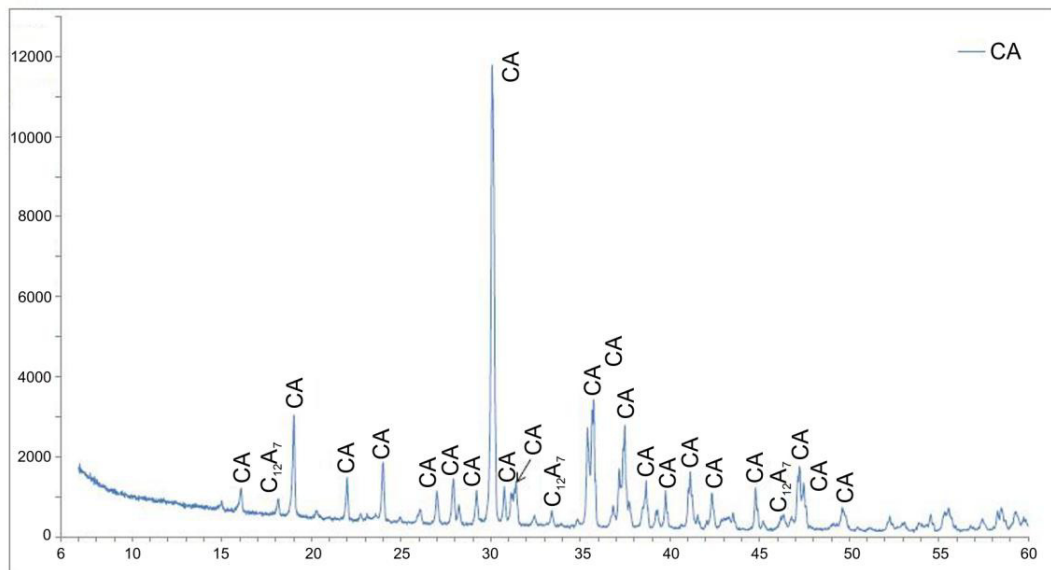


Fig. 2. XRD pattern of calcium monoaluminate CA.

3.3. Results

The results of phase composition determined by XRD method are presented in Fig. 3-6. In the case of hydration of alumina cement with addition of lithium carbonate significant amounts of C_2AH_8 hydrate can be observed just after 15 minutes since mixing of cement with water. Maximum content of that hydrate is achieved within 1 hour and decreases gradually up to complete disappearance after 28 days of hydration (fig. 4). During the hydration of alumina cement without admixture first C_2AH_8 hydrates can be indicated only after couple of hours since mixing with water and the intensity of peaks is significantly lower than that in the case of activation by lithium carbonate (fig. 3). In the paste not activated by admixture that hydrate is still present after 28 days of hydration.

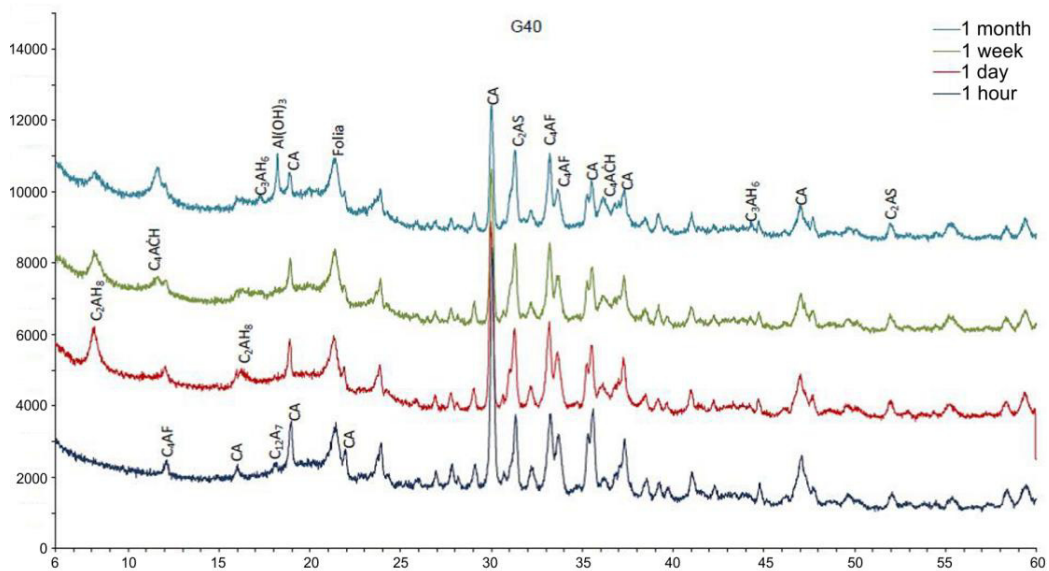


Fig. 3. Comparison of XRD patterns of alumina cement without admixture after 1 hour, 1, 7 and 28 days of hydration.

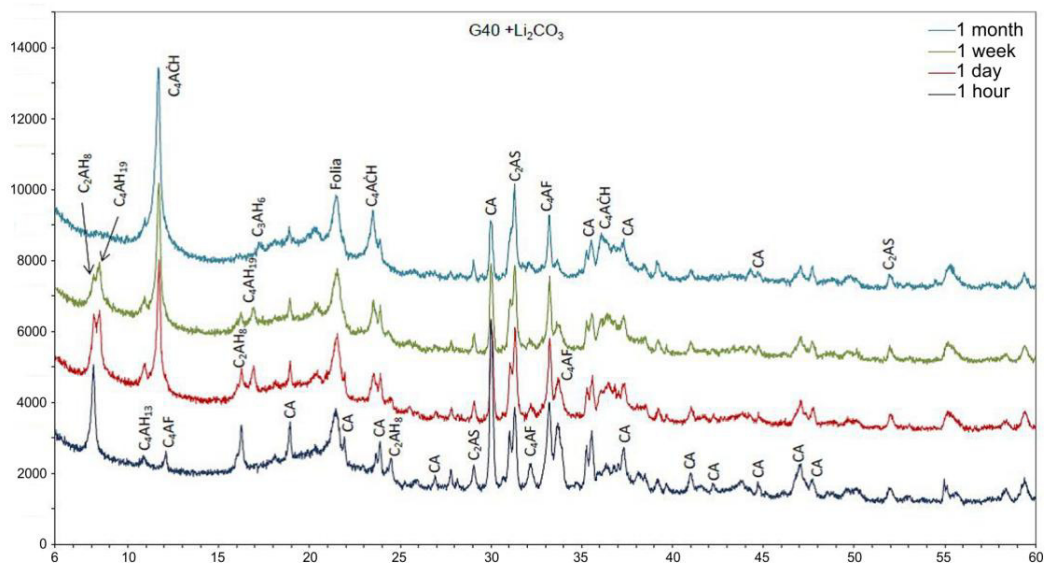


Fig. 4. Comparison of XRD patterns of alumina cement with addition of Li_2CO_3 after 1 hour, 1, 7 and 28 days of hydration.

In alumina cement paste with Li_2CO_3 hydrocalumite was present after one hour since mixing with water (fig.4), while that phase was absent in the paste without admixture (fig. 3). Hydrocalumite remains until 28 days. In cement with admixture significant amounts of $\text{C}_4\text{A}\cdot\text{H}_{11}$ carboaluminate are observed after 24 hours, while without admixture carboaluminate of definitely lower amounts was indicated only after 7 days since mixing with water. Similarly C_4AH_{19} can be identified after 24 hours of hydration, then it disappears between 7 and 28 days, while that phase is not observed in the paste without lithium carbonate.

Moreover, in the case of using lithium carbonate C_3AH_6 hydrogarnet can be indicated just after 7 days of hydration, while these hydrates are present in the paste without admixture only after 28 days. In both cases the reaction rate of gehlenite is not remarkable, however, comparing to the paste without admixture the increase of reaction rate of brownmillerite can be observed in the paste with addition of lithium carbonate after 7 days since mixing with water.

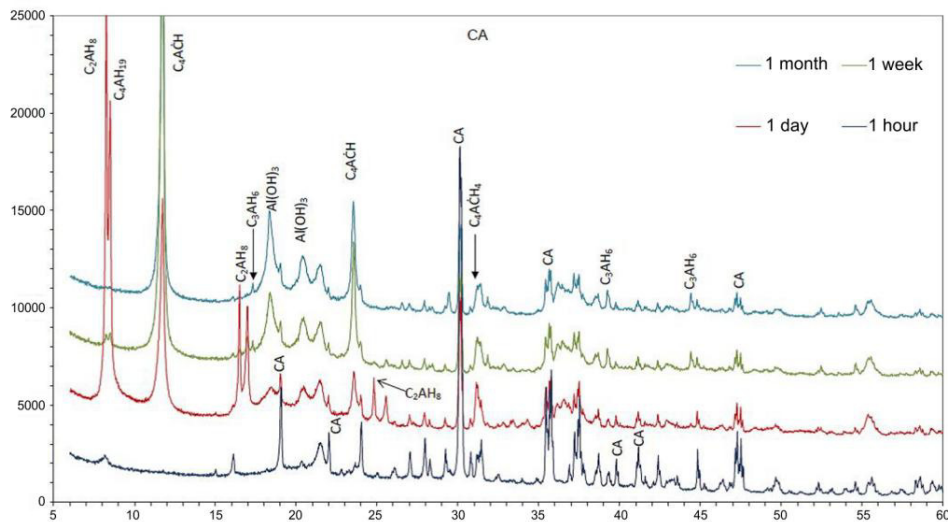


Fig. 5. Comparison of XRD patterns of calcium monoaluminate without admixture after 1 hour, 1, 7 and 28 days of hydration.

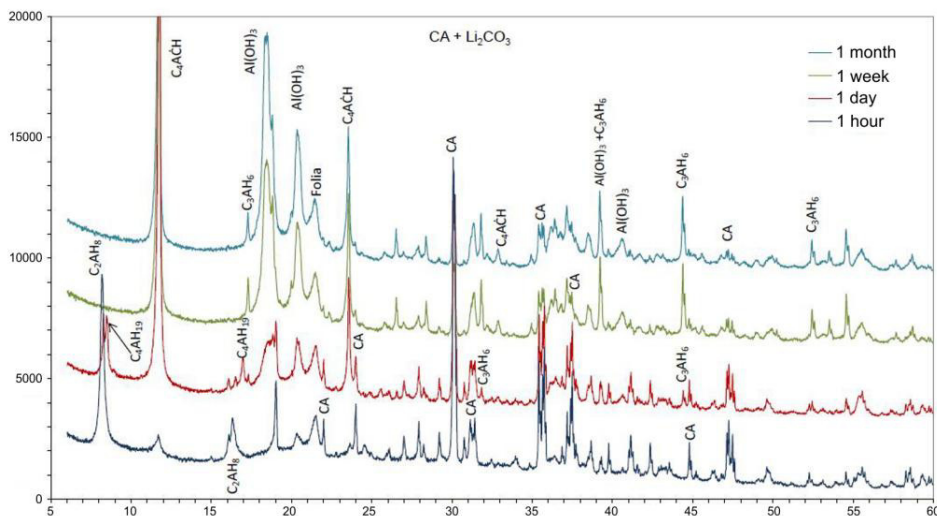


Fig. 6. Comparison of XRD patterns of calcium monoaluminate with addition of Li_2CO_3 after 1 hour, 1, 7 and 28 days of hydration.

In the paste of calcium monoaluminate with lithium carbonate addition (fig. 6) high amounts of C_2AH_8 can be indicated just after 1 hour since mixing with water and decrease of that phase during 24 hours up to complete disappearance before 7 days. In the case of paste without that admixture (fig. 5) the beginning of C_2AH_8 crystallization can be observed in the first hour of hydration, however, the maximum of intensity is found after 24 hours since mixing with water. In both pastes C_4AH_{19} can be identified after 24 hours, however, its amount is significantly higher in the paste without admixture. In the paste without lithium carbonate significant amounts of $C_4\tilde{A}H_{11}$ carboaluminate are observed after 24 hours too, while using admixture that phase can be found just after 1 hour since mixing with water with further content increase up to 24 hours. In the separate CA paste the crystals of gibbsite $Al(OH)_3$ can be indicated after 24 hours since mixing with water, while after activation by lithium carbonate gibbsite crystals can be identified just after 1 hour of hydration and the peak intensity is significantly higher.

In the paste without admixture C_3AH_6 hydrogarnet can be found after 7 days of hydration, while in the paste with lithium carbonate the corresponded peaks are noticeable just after 24 hours. The results of investigation of heat of hydration of alumina cement (HAC) without admixture and with the use of Li_2CO_3 are presented in Fig. 7 and 8.

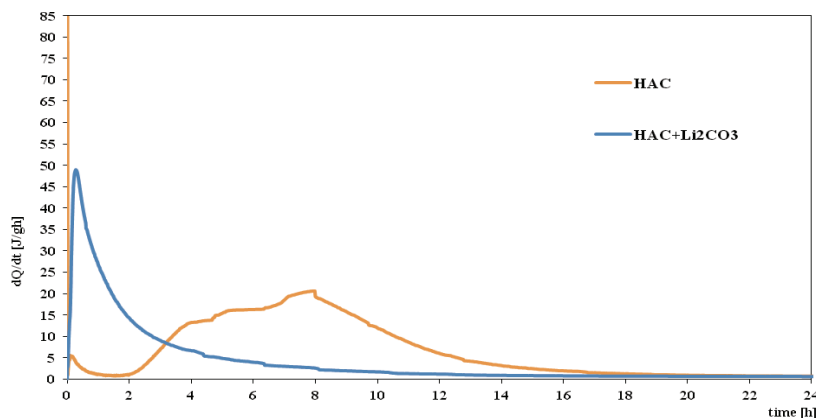


Fig. 7 Curves of speed of heat evolution of paste without admixture and with 0.3% addition of lithium carbonate.

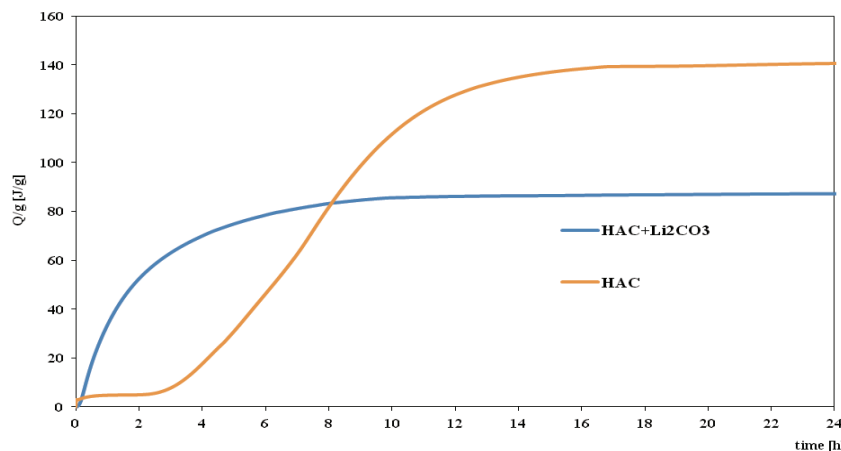


Fig. 8 Total amount of evolved heat of alumina cement paste without admixture and with 0.3% addition of lithium carbonate.

Microcalorimetric investigations of calcium monoaluminate allow to state that in the case of lithium carbonate addition (Fig. 7) the induction period becomes shorter and it is impossible to determine it due to the rapid setting. For separate CA the induction period takes about 2 hours. In the case of paste without admixture the maximum speed of heat evolution corresponds to the heat of wetting. It is important that in the case of paste with lithium carbonate addition the total amount of evolved heat is equal to about 80 J/g, while the amount of evolved heat during the hydration of paste without admixture is equal to almost 140 J/g (Fig. 8).

4. Conclusions

On the basis of performed investigations it can be stated that lithium carbonate has essential influence on the hydration course of alumina cement and its main constituent, i.e. CA calcium monoaluminate. However, hydration scheme in both cases is significantly different. In the case of cement as well as calcium monoaluminate lithium carbonate significantly accelerates crystallization of C_2AH_8 which is the first hydration product of cement phases and CA. Simultaneously the addition of lithium carbonate causes significant acceleration of hydrates conversion into C_3AH_6 hydrogarnet, described as unfavorable from strength point of view. In the case of alumina cement that conversion is poorly noticeable only after 28 days, after 7 days in the case of cement with lithium carbonate admixture and separate CA, while in the case of calcium monoaluminate with admixture just after 24 hours of hydration.

In the case of hydration of cement pastes with Li_2CO_3 the total amount of evolved heat is lower what most probably is related to inhibition of further hydration of grains coated by layer of rapidly growing reaction products. Most likely the inhibition of hydration and faster conversion of hydrates into hydrogarnets in the case of mortars with lithium carbonate addition lead to the strength decrease after 24 hours comparing to mortars without admixture discussed by Matusinovic, Curlin [6] and Niziurska, Małolepszy [9].

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